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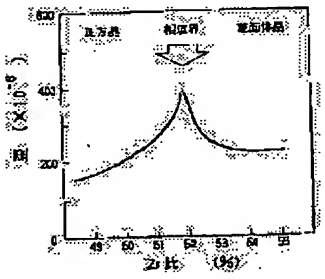
(54) FERROELECTRIC CERAMIC COMPOSITION

(57)Abstract:

PURPOSE: To provide a composition which uses a tetragonal system, is kept in good proportion to a strong electric field to cause large distortion, is not much affected by the temperature change of atmosphere and is excellent in durability.
CONSTITUTION: A ferroelectric ceramic composition is obtained by addition of SnO2, Nb2O5, SrO or BaO, etc., to PZT or a PZT system substance. Its crystal system is tetragonal wherein Zr ratio expressed as Zr/(Zr+Ti) is set to be at least 0.5mol% smaller than that of a phase boundary.



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CLAIMS

[Claim(s)]
[Claim 1] The ferroelectric porcelain constituent which it comes to add additives, such as SnO2, Nb 2O5, and SrO, BaO, to a PZT or PZT system, and the crystal system is made into tetragonal system, and is characterized by setting up Zr ratio expressed with Zr/(Zr+Ti) smaller at least 0.5 mole percents than Zr ratio of a phase boundary.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application] This invention relates to the amelioration technique of the ferroelectric porcelain constituent represented by electrostrictive ceramics.
[0002]
[Description of the Prior Art] When a strong electrical potential difference is impressed, the ferroelectric porcelain constituent (it abbreviates to a "ferroelectric" hereafter.) is adopted as mechanical components (actuator), such as a minute positioning device, using the property (inverse piezoelectric effect) in which a ferroelectric carries out distorted deformation.
[0003]
[Problem(s) to be Solved by the Invention] The above-mentioned ferroelectric takes the value of the phase boundary where the property at the time of generally the electrical potential difference of 1V (bolt) extent being impressed is made the best, and is application-ized.
[0004] However, the ferroelectric selected on the basis of the property near a phase boundary tends to be influenced of ambient temperature, and needs to perform suitable temperature compensation.
[0005] moreover, distorted as an actuator -- it is so good that a variation rate is large, and although he wants to raise applied voltage to 1kV for the reason, when such a high voltage is impressed, the conventional thing keeps that it is poor and there is no **** in practical use.
[0006] Then, the purpose of this invention is to offer the ferroelectric which combines the electric-field property of bearing the high voltage, endurance, and the good temperature characteristic.

[0007]

[Means for Solving the Problem and its Function] That the above-mentioned purpose should be attained, in a ferroelectric porcelain constituent, additives, such as SnO2, Nb 2O5, and SrO, BaO, are added to a PZT or PZT system, it becomes it, the crystal system is made into tetragonal system at it, and this invention is characterized by Zr ratio expressed with Zr/(Zr+Ti) being smaller than Zr ratio of a phase boundary at least 0.5 mole percents, and being set up.

[0008]

[Example] The result studied wholeheartedly that this invention person should improve the fault of the conventional PZT system ferroelectric, Are what added Nb2O5 of a minute amount, and SnO2 to the PZT system ferroelectric, and the ferroelectric of tetragonal system has a good electric-field property and endurance. And it is as finding out that the extremely characteristic ferroelectric porcelain constituent which is not looked at by the former that it cannot be easily influenced by the environmental temperature change is obtained, reaching this invention, and describing the detailed contents below. In addition, PZT is the abbreviated name of Pb(Zr, Ti) O3 crystalline.

[0009] Drawing 1 is the related Fig. of Zr ratio and a lattice constant in the ferroelectric containing the ferroelectric concerning this invention, manufactures two or more kinds of samples to which the Zr ratio was changed by the process of the usual electrostrictive ceramics centering on the constituent which added slight Nb2O5 and SnO2 to PZT, and asks these for a lattice constant by powder X-ray diffraction.

[0010] In addition, the above-mentioned Zr ratio is expressed with Zr/(Zr+Ti), and means the mole fraction of Zr contained in a constituent. On a notation, this is doubled 100 and it expresses with mole percent.

[0011] In drawing 1 , it is c= 4.113, a= 4.049A, and axial ratio (c/a) =1.0158 in the Zr ratio 49.0, and it turned out that a c-axis is small, an a-axis becomes large, an axial ratio (c/a) approaches 1.0, and the phase boundary which phase transition produces [Zr ratio] from ****** to ******** in the 52.0 to 52.25 neighborhood exists in an increment and ** of Zr ratio. It turned out that this to Zr ratio is tetragonal system or less in 52, and Zr ratio is a rhombohedral system or more in 52.25.

[0012] It carries out grinding of said sample to 1mm in thickness, drawing 2 is drawing showing Zr ratio of the ferroelectric containing the ferroelectric concerning this invention, and distorted relation, after it is able to be burned in a silver paste electrode, it impresses the electrical potential difference of 700V, and it shows what measured distortion using the non-contact type laser displacement gage and the strain gage.

[0013] As for distortion, according to drawing 2 , Zr ratio serves as max near 52.0-52.25. This is considered to be the presentation which the constituent near a phase boundary is soft and is easy to be distorted. And that the constituent near a phase boundary was adopted conventionally originates in distortion being large.

[0014] Drawing 3 (a) - (c) is drawing showing change of d constant when applying an electrical potential difference in the ferroelectric containing the ferroelectric concerning this invention, impresses the direct current voltage to 1.2kV/mm to the sample by which grinding was carried out to 1mm in said thickness, and plots piezo-electric d constant (it abbreviates to "d constant" hereafter.) computed based on distortion of 31 directions generated on this occasion.

[0015] Zr ratio can set drawing 3 (a) in the sample of 49.0-51.75, i.e., tetragonal system, d constant becomes large, so that Zr ratio is large, and as for d constant, 51.0 or less thing is mostly in direct proportion to the magnitude of electric field for Zr ratio. However, Zr ratio is decreasing with a peak of near 1kV/mm about 51.75.

[0016] drawing 3 (b) -- Zr ratio -- 52. -- to the sample 0 and 52.25, i.e., near a phase boundary, although d constant is large, it is decreasing from near 0.7kV/mm.

[0017] drawing 3 (c) -- Zr ratio -- 53. -- to the sample of 0 and 55.0, i.e., a rhombohedral system, while d constant is small, it cannot be said that it is in an increment and proportionality of electric field.

[0018] Drawing 3 (a) In order to obtain d constant which comparatively big d constant was obtained so

that – (c) might show, and is proportional to field strength, it is tetragonal system and Zr ratio can say that the sample of the 51.0 neighborhoods is desirable.
[0019] Drawing 4 is drawing showing the temperature effect nature of the ferroelectric containing the ferroelectric concerning this invention, and an axis of ordinate is a distortion rate in 60 degrees C when setting 0 degree C to 1.0, and increases rapidly to 1.2 or more times with a phase boundary and a rhombohedral system to a distortion rate being about 1.13 in tetragonal system. It is shown to change of ambient temperature that the sample of tetragonal system is the hardest to be influenced.
[0020] Drawing 5 is drawing showing the distorted rate of change by the electrical-potential-difference repetition durability test of the ferroelectric containing the ferroelectric concerning this invention, in the direct-current bias of 1.2 VK/mm and 1HZ, the distorted rate of change 1000 times, 10000 times, and after impressing 75000 times is shown, degradation progresses and a rhombohedral system is also accepted for degradation on a phase boundary.
[0021] On the other hand, extent of degradation [in tetragonal system] also after 75000 times is very small, and its endurance is large.
[0022] the ferroelectric porcelain constituent suitable from the above thing for an actuator — tetragonal system — and at least 0.5 mole percents from Zr ratio of a phase boundary — small — what was set as **** Zr ratio is suitable.
[0023] In addition, it is desirable that Zr ratio is set as the range of 50.0-51.50 in the example shown in drawing 3 (a) – (c) since generating distortion became small as it was shown in drawing 2 and drawing 3 (c), when each property tended to become unstable when a setup of Zr ratio was too close to the phase boundary, and a setup of Zr ratio was too small, and there was no **** in practical use.
[0024] In addition, the additive for a PZT system is good also as oxides, such as Nb2O5 and not only SnO2 but SrO, BaO, etc. Moreover, as for the ferroelectric of this invention, it is needless to say that it may be used as a ferroelectric of not only electrostrictive ceramics but a wide sense.
[0025]
[Effect of the Invention] Since the ferroelectric porcelain constituent of this invention is tetragonal system, it maintains good proportionality to strong electric field, produces a big distortion, and it is seldom influenced by the temperature change of an ambient atmosphere, and its endurance is good as stated above. Therefore, according to this invention, a reliable ferroelectric porcelain constituent can be offered by high power.

[Translation done.]

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] The related Fig. of Zr ratio and a lattice constant in the ferroelectric containing the ferroelectric concerning this invention
[Drawing 2] Drawing showing Zr ratio of the ferroelectric containing the ferroelectric concerning this invention, and distorted relation

[Drawing 3] Drawing showing change of d constant when applying an electrical potential difference in the ferroelectric containing the ferroelectric concerning this invention
[Drawing 4] Drawing showing the temperature effect nature of the ferroelectric containing the ferroelectric concerning this invention
[Drawing 5] Drawing showing the distorted rate of change by the electrical-potential-difference repetition durability test of the ferroelectric containing the ferroelectric concerning this invention

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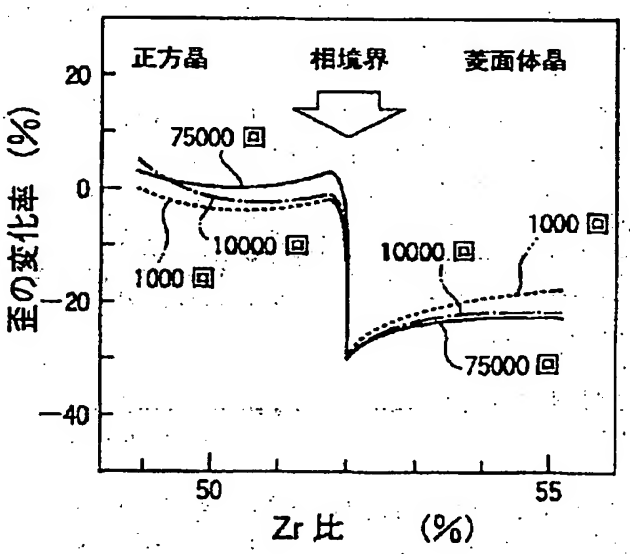
(54)【発明の名称】強誘電体磁器組成物

(57)【要約】

【構成】　ＰＺＴまたはＰＺＴ系にSnO_2，Nb_2O_5，ＳｒＯ，ＢａＯ等の添加物を加えてなり、その結晶系が正方晶系とされ、Ｚｒ／（Ｚｒ＋Ｔｉ）で表わされるＺｒ比が相境界のＺｒ比より少なくとも０．５モルパーセント小さく設定されたことを特徴とする強誘電体磁器組成物。

【効果】　本発明の強誘電体磁器組成物は、正方晶系なので強電界に対し良好な比例関係を保って大きな歪を生じ、雰囲気の温度変化にもあまり影響されず、且つ、耐久性良好である。



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【特許請求の範囲】

【請求項１】　ＰＺＴまたはＰＺＴ系にSnO_2，Nb_2O_5，ＳｒＯ，ＢａＯ等の添加物を加えてなり、その結晶系が正方晶系とされ、Ｚｒ／（Ｚｒ＋Ｔｉ）で表わされるＺｒ比が相境界のＺｒ比より少なくとも０．５モルパーセント小さく設定されたことを特徴とする強誘電体磁器組成物。

【発明の詳細な説明】

【０００１】

【産業上の利用分野】本発明は圧電セラミックスに代表される強誘電体磁器組成物の改良技術に関する。

【０００２】

【従来の技術】強い電圧を印加した時に強誘電体が歪変形する性質（逆圧電効果）を利用して微小位置決め装置等の駆動部（アクチュエータ）に強誘電体磁器組成物（以下、「強誘電体」と略す。）が採用されている。

【０００３】

【発明が解決しようとする課題】上記強誘電体は、一般に１Ｖ（ボルト）程度の電圧が印加された際の、特性が最も良いとされている相境界の値をとって応用化されている。

【０００４】しかし、相境界付近の特性を基準に選定された強誘電体は、周囲温度の影響を受けやすく、適当な温度補正を施す必要がある。

【０００５】又、アクチュエータとしては、歪変位が大きい程良く、その為に印加電圧を例えば１ＫＶにアップしたいが、従来のものはこのような高電圧を印加するとへたってしまい実用に供さない。

【０００６】そこで本発明の目的は、高電圧に堪える電界特性と、耐久性と、良い温度特性とを兼ね備えた強誘電体を提供することにある。

【０００７】

【課題を解決するための手段及び作用】上記目的を達成すべく本発明は、強誘電体磁器組成物をＰＺＴまたはＰＺＴ系にSnO_2，Nb_2O_5，ＳｒＯ，ＢａＯ等の添加物を加えてなり、その結晶系が正方晶系とされ、Ｚｒ／（Ｚｒ＋Ｔｉ）で表わされるＺｒ比が相境界のＺｒ比より少なくとも０．５モルパーセント小さく設定されたことを特徴とする。

【０００８】

【実施例】本発明者は、従来のＰＺＴ系強誘電体の欠点を改良すべく鋭意研究した結果、ＰＺＴ系強誘電体に微量のNb_2O_5，SnO_2を添加したもので且つ正方晶系の強誘電体は良好な電界特性及び耐久性を有し、且つ環境の温度変化に影響され難いという従来に見られない極めて特徴のある強誘電体磁器組成物が得られることを見い出し本発明に到達したものであり、その詳しい内容は以下に述べる通りである。なお、ＰＺＴは$Pb(Zr,Ti)O_3$結晶体の略称である。

【０００９】図１は本発明に係る強誘電体を含む強誘電体におけるＺｒ比と格子定数の関係図であり、ＰＺＴに僅かなNb_2O_5，SnO_2を加えた組成物を中心に、そのＺｒ比を変化させたところの複数種類の試料を通常の圧電セラミックスの製法で製造し、これらを粉末Ｘ線回析により、格子定数を求めたものである。

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【００１０】なお、上記Ｚｒ比はＺｒ／（Ｚｒ＋Ｔｉ）で表わされ、組成物中に含まれるＺｒのモル分率を意味する。表記上、これを１００倍してモルパーセントで表わす。

【００１１】図１において、Ｚｒ比４９．０でｃ＝４．１１３，ａ＝４．０４９オングストローム、軸比（ｃ／ａ）＝１．０１５８であり、Ｚｒ比の増加と伴に、ｃ軸は小さく、ａ軸は大きくなり、軸比（ｃ／ａ）が１．０に近づき、Ｚｒ比が５２．０～５２．２５付近で正方晶から菱面体晶へ相転移が生じる相境界が存在していることが分かった。このことからＺｒ比が５２以下では正方晶系であり、Ｚｒ比が５２．２５以上では菱面体晶系であることが分った。

【００１２】図２は本発明に係る強誘電体を含む強誘電体のＺｒ比と歪の関係を示す図であり、前記試料を厚さ１ｍｍに研削し、銀ペースト電極を焼き付けた後に７００Ｖの電圧を印加し、非接触式レーザ変位計及び歪ゲージを用いて歪を測定したものを示す。

【００１３】図２によれば、Ｚｒ比が５２．０～５２．２５の付近で歪は最大となる。これは相境界付近の組成物が軟かくて歪易い組成であると考えられる。そして、従来、相境界付近の組成物が採用されていたのは、歪が大きいことに起因している。

【００１４】図３（ａ）～（ｃ）は本発明に係る強誘電体を含む強誘電体に電圧を掛けた時のｄ定数の変化を示す図であり、前記厚さ１ｍｍに研削された試料に１．２ＫＶ／ｍｍまでの直流電圧を印加し、この際に発生した３１方向の歪に基づいて算出した圧電ｄ定数（以下、「ｄ定数」と略す。）をプロットしたものである。

【００１５】図３（ａ）はＺｒ比が４９．０～５１．７５、即ち正方晶系の試料におけるものであり、Ｚｒ比が大きい程ｄ定数が大きくなり、Ｚｒ比が５１．０以下のものは電界の大きさにｄ定数はほぼ正比例している。しかし、Ｚｒ比が５１．７５については１ＫＶ／ｍｍ付近をピークに減少傾向にある。

【００１６】図３（ｂ）はＺｒ比が５２．０，５２．２５、即ち相境界付近の試料に対するもので、ｄ定数は大きいものの、０．７ＫＶ／ｍｍ付近から減少傾向にある。

【００１７】図３（ｃ）はＺｒ比が５３．０，５５．０、即ち菱面体晶系の試料に対するもので、ｄ定数が小さいとともに電界の増加と比例関係にあるとは言えない。

【００１８】図３（ａ）～（ｃ）から分かるように比較的大きなｄ定数が得られ、且つ電界の強さに比例したｄ

定数を得るためには、正方晶系で且つ、Ｚｒ比が５１．０付近の試料が好ましいと言える。

【００１９】図４は本発明に係る強誘電体を含む強誘電体の温度影響性を示す図であり、縦軸は０℃を１．０としたときの６０℃における歪率であり、正方晶系では歪率が約１．１３であるのに対し、相境界及び菱面体晶系では１．２倍以上に急増する。雰囲気温度の変化に対し、正方晶系の試料が最も影響され難いことを示す。

【００２０】図５は本発明に係る強誘電体を含む強誘電体の電圧繰返し耐久試験による歪の変化率を示す図であり、１．２ＶＫ／ｍｍ，１ＨＺの直流バイアスを１０００回，１００００回及び７５０００回印加した後の歪の変化率を示すもので、相境界では劣化が進み、菱面体晶系も劣化が認められる。

【００２１】一方、正方晶系では７５０００回後でも劣化の程度は微少であり、耐久性が大きい。

【００２２】以上のことから、アクチュエータに好適な強誘電体磁器組成物は正方晶系で且つ相境界のＺｒ比から少なくとも０．５モルパーセント小さなＺｒ比に設定したものが好適である。

【００２３】なお、Ｚｒ比の設定が相境界に近すぎると各特性が不安定になりやすく、又、Ｚｒ比の設定が小さすぎると図２、図３（ｃ）に示した通り発生歪が小さくなり、実用に供さないので、図３（ａ）～（ｃ）に示した実施例においてはＺｒ比は５０．０～５１．５０の範囲に設定されることが好ましい。

【００２４】なお、ＰＺＴ系の為の添加物はNb_2O_5，SnO_2に限らずＳｒＯ，ＢａＯ等の酸化物としてもよい。又、本発明の強誘電体は圧電セラミックスに限らず広義の強誘電体として使用され得ることは勿論である。

【００２５】

【発明の効果】以上に述べた通り本発明の強誘電体磁器組成物は、正方晶系なので強電界に対し良好な比例関係を保って大きな歪を生じ、雰囲気の温度変化にもあまり影響されず、且つ、耐久性良好である。よって、本発明によれば高出力で信頼性の高い強誘電体磁器組成物が提供できる。

【図面の簡単な説明】

【図１】本発明に係る強誘電体を含む強誘電体におけるＺｒ比と格子定数の関係図

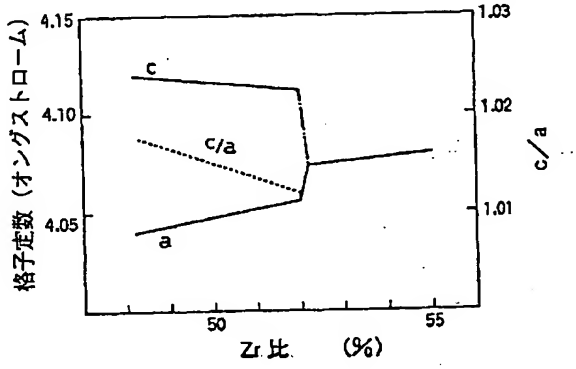
【図２】本発明に係る強誘電体を含む強誘電体のＺｒ比と歪の関係を示す図

【図３】本発明に係る強誘電体を含む強誘電体に電圧を掛けた時のｄ定数の変化を示す図

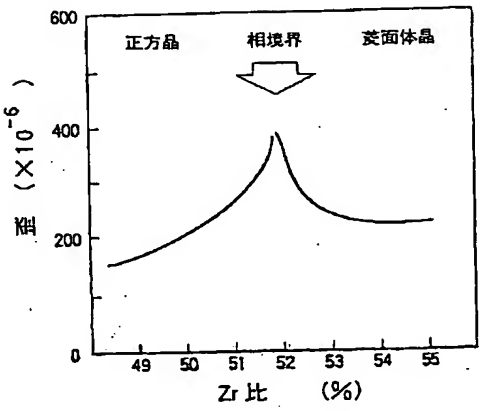
【図４】本発明に係る強誘電体を含む強誘電体の温度影響性を示す図

【図５】本発明に係る強誘電体を含む強誘電体の電圧繰返し耐久試験による歪の変化率を示す図

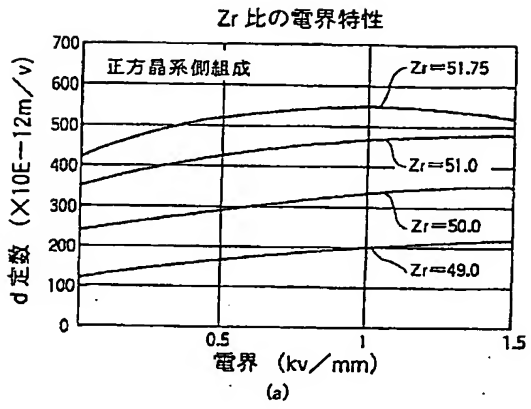
【図１】



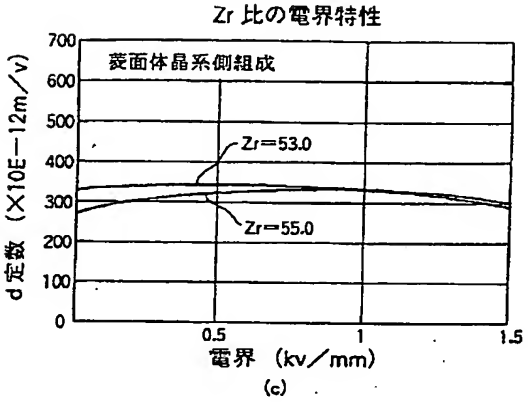
【図２】

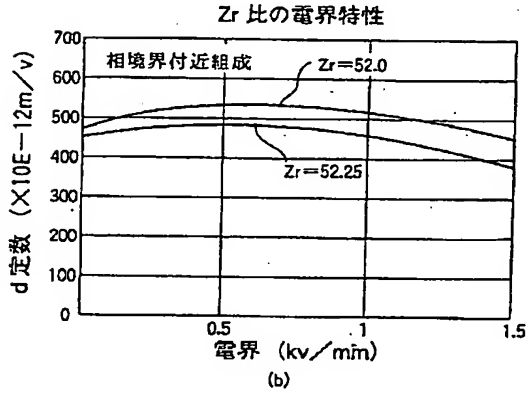


【図３】

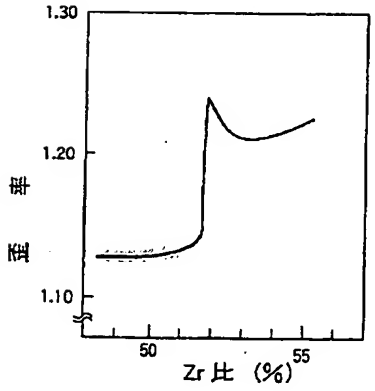


【図３】

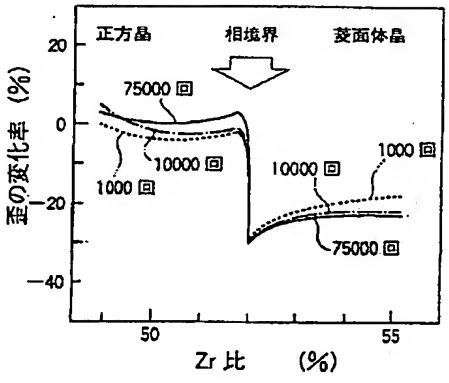




【図４】

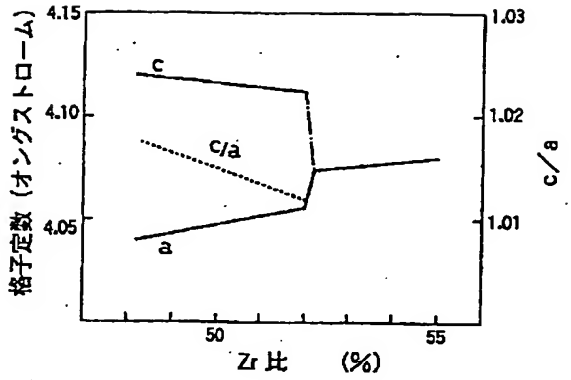


【図５】

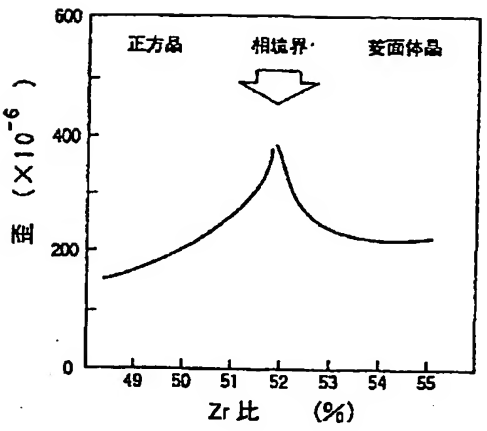


【手続補正書】
【提出日】平成５年５月２８日
【手続補正１】
【補正対象書類名】図面
【補正対象項目名】全図
【補正方法】変更
【補正内容】

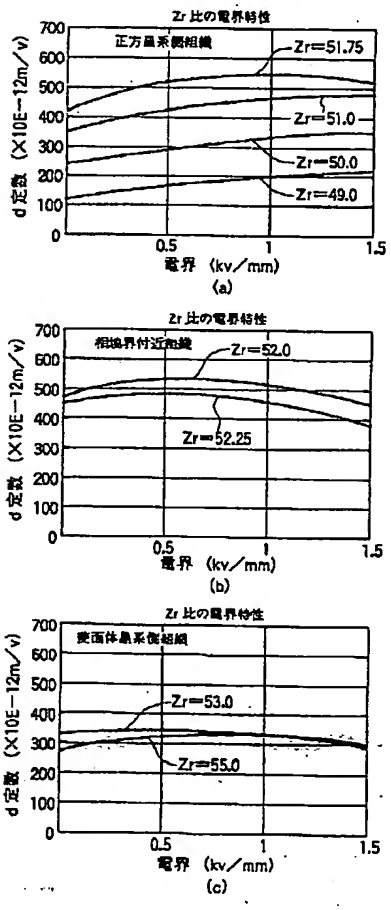
【図１】


格子定数（オングストローム）
4.15
4.10
4.05
c
c/a
a
1.03
1.02
1.01
c/a
50
55
Zr 比　(%)

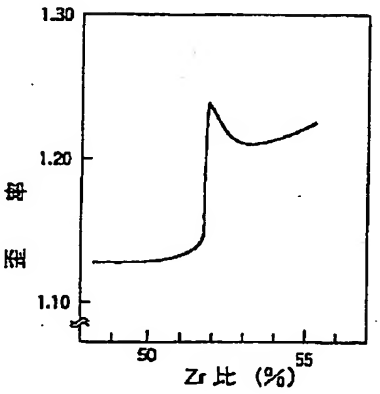
【図２】


600
400
200
0
正方晶
相境界
菱面体晶
歪（×10⁻⁶）
49
50
51
52
53
54
55
Zr 比　(%)

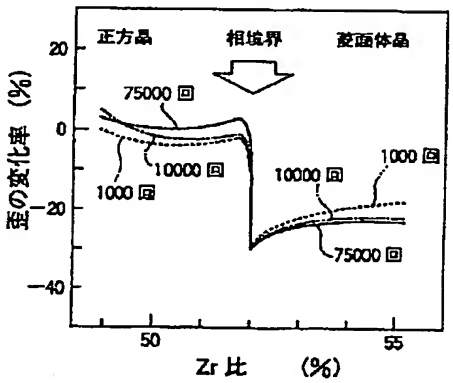
【図３】


Zr 比の電界特性
正方晶系側組織
Zr=51.75
Zr=51.0
Zr=50.0
Zr=49.0
d 定数（X10E−12m/v）
電界（kv/mm）
(a)
Zr 比の電界特性
相境界付近組織
Zr=52.0
Zr=52.25
(b)
Zr 比の電界特性
菱面体晶系側組織
Zr=53.0
Zr=55.0
(c)

【図４】


1.30
1.20
1.10
歪
50
55
Zr 比　(%)

【図５】


正方晶
相境界
菱面体晶
歪の変化率（%）
20
0
−20
−40
75000 回
10000 回
1000 回
50
55
Zr 比　(%)